

Department of Water Resources



684 Winder Highway • Lawrenceville, GA 30045-5012
678.376.6700
www.gwinnettcounty.com

gwinnett county

July 15, 2016

Mr. Kevin Collins
Georgia Environmental Protection Division Land Protection Branch
2 Martin Luther King, Jr. Drive SE
Suite 1456 East
Atlanta, Georgia 30334

Subject: July 2016 Semi-Annual Voluntary Remediation Program Progress Report
North Berkeley Lake Road Site (HSI No. 10844)
Duluth, Gwinnett County, Georgia

Dear Mr. Collins:

This Progress Report documents the activities completed for the North Berkeley Lake Road Site, also referred to as Fire Station 19, in Duluth, Georgia from January 2016 through June 2016. This report constitutes the third semi-annual progress report and follows the schedule outlined in the Georgia Environmental Protection Division's (EPD's) letter dated January 15, 2015.

This Progress Report includes the following:

- Work Performed This Period;
- Work Anticipated for the Next Period;
- Schedule; and
- Professional Certification.

Work Performed This Period

Limited work was performed during the current reporting period. Gwinnett County and its consultant, CDM Smith, believe that the horizontal and vertical delineation of arsenic in soil and groundwater is complete, as detailed in the Corrective Action Plan (CDM Smith, October 2014) previously submitted to EPD.

On March 30, 2016, an article titled "Predicting oral relative bioavailability of arsenic in soil from in vitro bioaccessibility" was published in the Journal of Toxicology and Environmental Health. This article is provided in **Attachment A** and outlines use of a newer model for evaluating the bioavailability of arsenic. This research was funded by the U.S. Environmental Protection Agency (EPA). Similar to the older model, and if approved for use, the results of this method would have a significant impact on the final Risk Reduction Standards (RRSs) for Fire Station 19. Lower RRSs are likely to mitigate potential costs and secondary impacts associated with addressing arsenic in soil while being sufficiently protective. For example, one method currently under consideration for Fire

Station 19 is to pave the open areas of the site, thus preventing access to arsenic in soil for the trespasser and onsite worker scenarios. This method, while less expensive than excavation and offsite disposal, is still costly and has negative stormwater and aesthetic impacts.

Gwinnett County and CDM Smith understand through contacts at EPA that formal EPA approval of the alternative arsenic bioavailability method is only a matter of time. However, it seems unlikely that approval will occur before January 2017, the deadline for a final remediation plan for Fire Station 19. As such, Gwinnett County requests consideration of a one year extension for submittal of a final remediation plan. This request for an extension will not affect the compliance status report deadline of July 15, 2020 previously established for this project. We believe that potential risks of exposure to arsenic in soil in the interim are currently mitigated by:

1. Use of the property as a fire station.
2. Fire personnel being on site 24 hours a day (limited potential for trespassing).
3. Fire personnel having been informed of arsenic in soil and asked to limit any contact with soil on the property.
4. Gwinnett County disallowing any non-fire related training or operations to be conducted on the property.

Work Anticipated for the Next Period

Gwinnett County and CDM Smith will continue monitoring EPA progress and approvals regarding the use of bioaccessibility methods for setting arsenic cleanup levels. If an extension for submission of a final remediation plan is not granted by EPD, Gwinnett County and CDM Smith will proceed with preparation of a final remediation plan to be submitted on or before January 15, 2017.

Schedule

As previously noted, Gwinnett County has requested a one-year extension for submittal of a final remediation plan with proposed cleanup levels and a cost estimate. If granted by EPD, these items will be submitted to EPD for review on or before January 15, 2018. If not granted by EPD, these items will be submitted to EPD for review on or before January 15, 2017.

Professional Certification

Attachment B contains the professional certification and summary of incurred professional engineer and geologist hours for the period from January 1, 2016 through June 30, 2016.

Page 3

Georgia Department of Natural Resources, EPD; Mr. David Brownlee
North Berkeley Lake Road Site (HSI No. 10844) – July 2016 Semi - Annual
July 15, 2016

If you have any questions regarding this Progress Report, please do not hesitate to contact me at (678) 376-6953 or richard.shoeck@gwinnettcounty.com.

Sincerely,

GWINNETT COUNTY DEPARTMENT OF WATER RESOURCES

Richard Schoeck, P.E., PMP
Division Director of Project Controls

Attachment

cc: Tom Duffey, CDM Smith
Forrest Fields, Gwinnett County
J.C. Lan, Gwinnett County
John Reichling, CDM Smith
Andrew Romanek, CDM Smith



Journal of Toxicology and Environmental Health, Part A

Current Issues

ISSN: 1528-7394 (Print) 1087-2620 (Online) Journal homepage: <http://www.tandfonline.com/loi/uteh20>

Predicting oral relative bioavailability of arsenic in soil from in vitro bioaccessibility

Gary L. Diamond, Karen D. Bradham, William J. Brattin, Michele Burgess, Susan Griffin, Cheryl A. Hawkins, Albert L. Juhasz, Julie M. Klotzbach, Clay Nelson, Yvette W. Lowney, Kirk G. Scheckel & David J. Thomas

To cite this article: Gary L. Diamond, Karen D. Bradham, William J. Brattin, Michele Burgess, Susan Griffin, Cheryl A. Hawkins, Albert L. Juhasz, Julie M. Klotzbach, Clay Nelson, Yvette W. Lowney, Kirk G. Scheckel & David J. Thomas (2016) Predicting oral relative bioavailability of arsenic in soil from in vitro bioaccessibility, *Journal of Toxicology and Environmental Health, Part A*, 79:4, 165-173, DOI: [10.1080/15287394.2015.1134038](https://doi.org/10.1080/15287394.2015.1134038)

To link to this article: <http://dx.doi.org/10.1080/15287394.2015.1134038>



[View supplementary material](#)



Published online: 30 Mar 2016.



[Submit your article to this journal](#)



Article views: 14



[View related articles](#)



[View Crossmark data](#)

Full Terms & Conditions of access and use can be found at
<http://www.tandfonline.com/action/journalInformation?journalCode=uteh20>

Predicting oral relative bioavailability of arsenic in soil from in vitro bioaccessibility

Gary L. Diamond^a, Karen D. Bradham^b, William J. Brattin^a, Michele Burgess^c, Susan Griffin^d, Cheryl A. Hawkins^c, Albert L. Juhasz^e, Julie M. Klotzbach^a, Clay Nelson^b, Yvette W. Lowney^f, Kirk G. Scheckel^g, and David J. Thomas^h

^aSRC, Inc., North Syracuse, New York, USA; ^bU.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Research Triangle Park, North Carolina, USA; ^cU.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, Science Policy Branch, Washington DC, USA; ^dU.S. Environmental Protection Agency, Denver, Colorado, USA;

^eCentre for Environmental Risk Assessment and Remediation, University of South Australia, Adelaide, South Australia, Australia; ^fExponent, Inc., Boulder, Colorado, USA; ^gU.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, Ohio, USA; ^hU.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Research Triangle Park, North Carolina, USA

ABSTRACT

Several investigations have been conducted to develop in vitro bioaccessibility (IVBA) assays that reliably predict in vivo oral relative bioavailability (RBA) of arsenic (As). This study describes a meta-regression model relating soil As RBA and IVBA that is based upon data combined from previous investigations that examined the relationship between As IVBA and RBA when IVBA was determined using an extraction of soil in 0.4 M glycine at pH 1.5. Data used to develop the model included paired IVBA and RBA estimates for 83 soils from various types of sites such as mining, smelting, and pesticide or herbicide application. The following linear regression model accounted for 87% of the observed variance in RBA ($R^2 = .87$): $RBA(\%) = 0.79 \times IVBA(\%) + 3$. This regression model is more robust than previously reported models because it includes a larger number of soil samples, and also accounts for variability in RBA and IVBA measurements made on samples collected from sites contaminated with different As sources and conducted in different labs that have utilized different experimental models for estimating RBA.

ARTICLE HISTORY

Received 28 September 2015
Accepted 17 December 2015

A recent compilation of data from a variety of arsenic (As)-contaminated sites demonstrated that oral bioavailability of As in soil tends to be lower than that of water soluble sodium arsenite (U.S. Environmental Protection Agency [EPA], 2012a, 2012b). Expressed as relative oral bioavailability (RBA, the percent ratio of bioavailability of As in soil to that of dissolved sodium arsenite), the mean and 95th percentile RBA values for more than 100 soil samples were 30% and 60%, respectively. Many factors affect the bioavailability of As in soil, including chemical form of As, as well as physical and chemical characteristics of As-bearing soil particles, and these factors are known to vary both within and between sites (Bradham et al., 2011; Brattin et al., 2013; Roberts et al., 2007; Ruby et al., 1999; Scheckel et al., 2009). The U.S. Environmental Protection Agency (EPA) recommended that site-specific

assessments of soil As RBA be performed where such assessments are deemed feasible and valuable for improving the characterization of risk at the site (U.S. EPA, 1989, 2007a, 2007b).

Currently accepted methods for assessing oral RBA of soil As require animal bioassays (U.S. EPA, 2012b). The time and expense of animal bioassays have prompted interest in developing more rapid and less expensive in vitro bioaccessibility (IVBA) assays that may be employed to reliably predict oral RBA of soil As (Bradham et al., 2011, 2015; Brattin et al., 2013; Denys et al., 2012; Juhasz et al., 2007a, 2007b, 2009, 2011, 2014a, 2014b; Makris et al., 2008; Medlin, 1997; Roberts et al., 2007; Rodriguez et al., 1999; Ruby et al., 1996; Wragg et al., 2011). IVBA assays measure the solubility of As when soil is incubated in an aqueous solution that often is intended to mimic temperature, pH,

CONTACT Gary Diamond  diamond@srcinc.com  SRC, Inc., 8191 Cedar St., Akron, NY 14001, USA.

 Supplemental data for this article can be accessed at [10.1080/15287394.2015.1134038](http://dx.doi.org/10.1080/15287394.2015.1134038) and include brief descriptions of in vivo RBA assay methods, IVBA and RBA estimates, and soil arsenic concentrations for all soil samples considered in this analysis (Table S-1), and plots of data from each laboratory (Figures S-1–S-3).

© 2016 Taylor & Francis

and other compositional characteristics of gastrointestinal tract (GIT) fluids. The underlying assumption for the use of an IVBA assay to predict *in vivo* RBA is that solubility of a chemical in GIT fluids is an important determinant of GIT absorption; therefore, it is expected that IVBA will be highly correlated with RBA measured *in vivo*. Testing this assumption requires that regression models relating IVBA and RBA be evaluated with paired measurements of IVBA and RBA conducted on a variety of soils that reflect a range of As concentrations, soil types, and chemical forms of arsenic that occur in soil at affected sites.

This study focused on an IVBA assay that was developed for and is currently used widely in the assessment of lead RBA (Drexler and Brattin, 2007). The assay involves a gastric-phase extraction of soil in a relatively simple extraction medium (0.4 M glycine buffer at pH 1.5 ± 0.5). Several investigations found that the 0.4 M glycine/pH 1.5 assay provided estimates of As IVBA that were highly correlated with *in vivo* As RBA measured in mice and swine (Bradham et al., 2011, 2013; Brattin et al., 2013; Juhasz et al., 2009, 2014a). However, each of these investigations derived a unique regression model relating IVBA and RBA. Several factors may have contributed to differences in the regression models derived in each study, including use of different animal bioassays for measuring RBA, interlaboratory differences in IVBA measurement error, and variability in soil characteristics or As speciation of the samples assayed by each lab. Although one could opt to select a specific regression model from a given study for human health risk assessment applications, this is unlikely to be optimal because there are no apparent distinguishing quality or conceptual factors that may serve as a basis for deciding which regression model more accurately predicts soil As RBA in humans.

An alternative to selecting a single study as the basis for a regression model is to derive a model based on collective data from multiple investigations. This single meta-model would incorporate the observed variability in the IVBA–RBA relationship found in multiple studies, and would provide more realistic prediction limits for assessing uncertainty in RBA estimates utilized in risk assessment. Accordingly, in this analysis, data from multiple investigations were

combined into an aggregate (pooled) data set and a regression model was derived for predicting RBA from IVBA measured in the 0.4 M glycine/pH 1.5 assay. The resulting pooled regression model is more robust than previously reported models because it includes both a larger number of soil samples and a wider variety of sources of As contamination such as mining, smelting, and herbicides or pesticides. In addition, the pooled model also accounts for variability in RBA and IVBA measurements performed in different labs that utilized different experimental models for estimating RBA.

Methods

Data included in the meta-analysis

Studies that contributed data to the meta-analysis found good correlations ($R^2 > .6$) between As IVBA and RBA in soils, when IVBA was assessed with the 0.4 M glycine/pH 1.5 assay (Bradham et al., 2011, 2015; Brattin et al., 2013; Juhasz et al., 2009, 2014a). From these investigations, only data from authentic site samples were selected for meta-analysis. Samples prepared by adding As to soil in the lab, with or without aging, were excluded from consideration. Investigators for these studies were contacted and each agreed to provide individual sample data for the meta-analysis, including confidence estimates for each RBA and IVBA value. Data from the individual labs provided the following numbers of IVBA–RBA pairs: lab A, $n = 40$ (Bradham et al. 2011, 2013, 2015); Lab B, $n = 19$ (Brattin et al. 2013); and lab C, $n = 24$ (Juhasz et al. 2009, 2014a).

IVBA assay methods

All IVBA assays followed the extraction protocol described in U.S. EPA (2012c). Each soil sample was dried and sieved (<250 µm), and 1 g sieved soil was incubated with constant agitation (end-over-end rotation) at 37°C for 1 h in 100 ml solvent made up of 0.4 M glycine, pH 1.5. Arsenic in the soil was quantified by Instrumental Neutron Activation Analysis, or by microwave-assisted digestion (EPA SW-846 Method 3051A), with analysis by inductively coupled plasma–atomic emission spectrometry (ICP-AES; EPA SW-846 Method 6010c) (U.S.



EPA, 2007c) or ICP–mass spectrometry (ICP-MS; EPA SW-846 Method 6020A) (U.S. EPA, 2007d). Arsenic in the extraction fluid was measured by ICP-MS (EPA SW-846 Method 6020) or inductively coupled plasma-optical emission spectroscopy (ICP-OES, EPA SW-846 Method 6010c).

In vivo RBA assay methods

In vivo RBA assays used in the various studies have been published and are described briefly in the Supplemental Data. Assays conducted in C57BL/6 mice were performed as reported in Bradham et al. (2011) (referred to in this report as the mouse urinary excretion fraction or UEF assay). In vivo RBA assays in juvenile swine reported in Brattin et al. (2013) were performed as described in Brattin and Casteel (2013) (referred to in this report as the swine UEF assay). In vivo RBA assays conducted in juvenile swine, reported in Juhasz et al. (2009, 2014b), were performed as described in Rees et al. (2009) (referred to in this report as the swine area under the curve or AUC assay).

Statistical analyses

All statistical analyses were performed using SAS/STAT software, Version 9.3 of the SAS System for Windows SAS software or Aegis Technologies Advanced Continuous Simulation Language (acsIX). A *p* value ≤.05 was considered significant in all comparisons.

Two types of regression analyses were performed on these data. Preliminary regression modeling relied on ordinary least squares (OLS) linear regression. These preliminary analyses were used to identify major explanatory variables for RBA, outliers, and regression diagnostics (e.g., heteroscedasticity, normality of residuals). Final regression modeling of the pooled data used weighted least squares regression. This approach allowed incorporation of uncertainty in individual IVBA and RBA estimates into the regression model.

Linear regression was performed using the general linear model (SAS PROC GLM), with RBA as the dependent variable. The general linear model used in these analyses is given in Eq. (1):

$$Y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \beta_3 X_{i3} + \epsilon_i \quad (1)$$

where β_0 is the intercept and β_1 is the slope coefficient for IVBA (X_1). Because each lab estimated RBA using different animal bioassays, an explanatory categorical variable (*laboratory*) was included in the general linear model (β_2, X_2 in Eq. (1)). The predominant source of As (e.g., ore or ore processing, pesticide application, herbicide application) at the site from which the soil sample was collected was also explored as a categorical variable (*As source*, β_3, X_3 in Eq. (1)). Requirements for homoscedasticity and normality of errors were tested using White's test (SAS PROC REG/SPEC) and the Shapiro-Wilks statistic (SAS PROC REG/UNIVARIATE), respectively. Pooled data were tested for heterogeneity of slopes for different labs (SAS PROC GLM, X^*GROUP effect). Studentized residuals (>3 or <-3) were used to identify statistical outliers. Cook's *D* statistic ($>4/n$) was used to identify influential outliers.

Based on the results of the multivariate regression analysis, the model was reduced to a monovariate, with IVBA as the independent variable (see Results section for explanation). Weighted linear regression was performed with uncorrelated weights assigned to each soil (W_i) calculated from Eq. (2):

$$W_i = \frac{w(X_i) w(Y_i)}{w(X_i) + (Y_i) (\beta^2)} \quad (2)$$

where $w(X_i)$ are IVBA weights ($1/SD_i^2$), $w(Y_i)$ are RBA weights ($1/SE_i^2$), and β is the slope of the linear regression line fit by minimizing the weighted sum of squared residuals (Thirumalai et al., 2011; York et al., 2004).

Results

Attributes of the data set

The data set is summarized in Table 1 and individual sample data are presented in the Supplemental Data (Table S-1). As shown, there was wide variability in As concentrations and values for IVBA and RBA values across the 83 samples. This wide variability is important to help constrain and define the model. The correlation between IVBA and RBA data from each lab are shown in the Supplemental Data (Figures S-1–S-3). Means of IVBA or RBA from

Table 1. Summary of IVBA and RBA Estimates Used in the Meta-Analysis.

	Data source			
	Lab A	Lab B	Lab C	Pooled
RBA assay				
Sample N	Mouse UEF 40	Swine UEF 19	Swine AUC 24	Mouse, swine 83
Soil As (ppm)				
Mean	790	670	664	726
SD	1214	852	577	978
Median	455	383	468	401
Range	108, 6899	181, 3857	42, 2270	42, 6899
IVBA (%)				
Mean	25.0	29.5	29.0	27.2
SD	19.5	18.4	23.0	20.2
Median	18.2	22.0	18.4	19.0
Range	0.0, 74.3	6.0, 78.0	43.8, 80.0	0.0, 80.0
RBA (%)				
Mean	24.3	37.3	29.3	28.7
SD	13.9	12.9	21.1	16.7
Median	21.4	40.3	21.2	23.8
Range	1.9, 51.6	17.8, 60.2	7.0, 80.5	1.9, 80.5

Note. As, arsenic; IVBA, in vitro bioaccessibility; RBA, relative bioavailability; SD, standard deviation; UEF, urinary excretion fraction; AUC, area under the curve.

sites contaminated predominantly from ore or ore processing (gossan, mining, smelting), pesticides (orchards and livestock dip sites), or herbicides (railway corridors) were not significantly different (Table 2).

Preliminary evaluations

A preliminary regression analysis of pooled data using OLS regression was used to identify

important independent variables in the regression model. The effect of interlab variability was explored with multiple regression analysis in which laboratory was included in the regression model as a categorical variable representing the lab source of each IVBA-RBA observation. The effect of predominant source of As contamination was included in the regression model as a categorical variable (As source) representing ore or ore processing, pesticide application, or herbicide application. Laboratory, As source, and IVBA were found to be significant variables in the pooled model and together accounted for approximately 85% of the variance in RBA ($R^2 = .85$). A test of heterogeneity of slopes for data from each laboratory or As source was not significant, indicating that combined data may be described by a common slope. When IVBA, laboratory, and As source were included in the model, the regression coefficient (slope) for IVBA was 0.71 (± 0.04 SE) and the intercept was 12.4 (± 2.2 SE). When laboratory was excluded from the model, leaving As source and IVBA as the sole explanatory variables, R^2 decreased from .85 to .79. When both As source and laboratory were excluded from the model, leaving IVBA as the sole explanatory variable, R^2 was .76. This suggests that approximately 76% of the variance in RBA was attributable to IVBA and approximately 9% was attributed to As source (6%) and laboratory (3%). These results indicate that, for this data set, IVBA is the dominant

Table 2. Summary of IVBA and RBA Estimates by Primary Contamination Source.

	Primary source of contamination		
	Ore or ore processing ^a	Insecticide application ^b	Herbicide application ^c
Sample N	52	21	10
Soil As (ppm)			
Mean	899	450	404
SD	1183	280	393
Median	586	364	252
Range	88, 6899	200, 1221	42, 1114
IVBA (%)			
Mean	27.8	20.8	37.0
SD	21.3	13.7	23.0
Median	20.1	18.0	34.9
Range	0.0, 78.4	5.7, 55.4	10.5, 80.0
RBA (%)			
Mean	27.3	28.1	37.5
SD	16.4	13.3	23.1
Median	23.3	29.1	30.0
Range	1.9, 70.5	10.1, 52.8	10.1, 80.5

Note. As, arsenic; IVBA, in vitro bioaccessibility; RBA, relative bioavailability; SD, standard deviation.

^aGossan, mining, smelting.

^bOrchards, livestock dip sites.

^cRailway corridors.



variable determining RBA. On this basis, the monovariate model with only IVBA as the explanatory variable was adopted for estimating parameter values for the regression relationship between IVBA and RBA.

Final model fitting

Development of the final model used weighted regression in which the squared error between each observed and predicted RBA value is weighted by the uncertainty in the measured RBA and IVBA values (estimates having higher uncertainty were assigned smaller weights). Weighting for RBA uncertainty is needed because of the relatively wide range of uncertainties in reported RBA values (0.3–19.9%). Ratios of SE/mean RBA also appeared to vary across labs, although mean SE/mean ratios were not significantly different: A, 0.07 (± 0.034 SD), B, 0.082 (± 0.039 SD), and C, 0.2 (± 0.13 SD). Uncertainty in IVBA values was generally smaller and more uniform than RBA. Mean coefficients of variation (CV, ratio of mean/standard deviation) for IVBA in each lab were <5%, typical for the As IVBA assay (Brattin et al., 2013). Mean IVBA CVs were similar across and lower than mean/SE ratios for RBA: A, 0.04, B, 0.05, and C, 0.021. The weighted regression model is shown in Figure 1. The estimated slope is 0.79 ± 0.01 (SE) and intercept is 3 ± 0.1 (SE). The equation of the model is

$$\text{RBA}(\%) = 0.79 \times \text{IVBA}(\%) + 3 \quad (3)$$

This model explains approximately 87% of the variance in RBA (weight-adjusted $R^2 = .87$). The 95% prediction limit for a single RBA measurement was $\pm 19\%$ RBA.

The model shown in Figure 1 excludes one observation that was an influential outlier based on its Studentized residual = -3.6 and Cooks D statistic ($= 0.12 > 4/n (= 0.05)$) (sample number 34, Supplemental Data, Table S-1). The IVBA for this sample was 41.7%, and its RBA was 6.8%. The high IVBA/RBA ratio for this soil (6.1) exceeded ratios for all other soils (range: 0.25–1.6). Excluding this sample exerted little

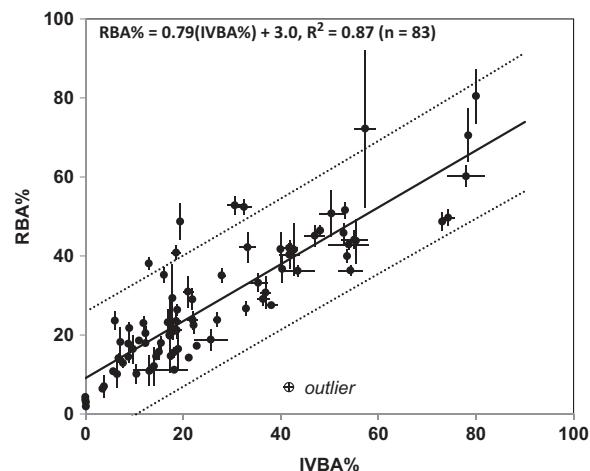


Figure 1. Weighted linear regression of RBA and IVBA based on data pooled from three laboratories. Points are observations $\pm \text{SE}$ (RBA) and $\pm \text{SD}$ (IVBA). The solid line is the weighted regression model. Dotted lines are 95% prediction limits for the weighted model. The data point labeled *outlier* was not used in fitting regression models.

effect on the pooled regression model. With the observation included, the regression model ($R^2 = .85$) had slope $0.76 (\pm 0.01)$ and intercept $3 (\pm 0.1 \text{ SE})$.

Discussion

Several investigations have been conducted by scientists worldwide to develop IVBA assays that reliably predict in vivo RBA of As (Bradham et al., 2011; 2015; Brattin et al., 2013; Roberts et al., 2007; Denys et al., 2012; Juhasz et al., 2007a, 2007b, 2009, 2011, 2014a, 2014b; Makris et al., 2008; Medlin, 1997; Rodriguez et al., 1999; Ruby et al., 1996; Wragg et al., 2011). This meta-analysis builds on published studies that examined the relationship between IVBA and RBA of As in soil when IVBA was measured from an extraction of soil in 0.4 M glycine at pH 1.5 (Bradham et al., 2011; 2015; Brattin et al., 2013; Juhasz et al., 2009; 2014a). Using different in vivo RBA bioassays, these studies found that the 0.4 M glycine/pH 1.5 IVBA assay, originally developed for predicting in vivo RBA of soil lead (U.S. EPA, 2012c), performed well in predicting in vivo As RBA in mice and swine. The Juhasz et al. (2009, 2014a) studies compared the performance of existing IVBA assays, whereas Brattin et al. (2013) optimized IVBA assay conditions de novo and found

that optimal performance was achieved with 0.4 M glycine/pH 1.5. Performance of the IVBA assay (R^2) was not improved at higher pH or with addition of phosphate, hydroxylamine, or hypochlorite, or with increased buffer strength. In addition, when 4 independent labs used the 0.4 M glycine/pH 1.5 assay to estimate IVBA of 12 identical soil samples, inter-ab variation in mean IVBA estimates was less than 5% (mean 1.7%; Brattin et al., 2013). Collectively, these studies provided evidence for reliability and reproducibility of the 0.4 M glycine/pH 1.5 IVBA assay for predicting soil As RBA.

Each of the investigations just described derived a unique regression model relating IVBA and RBA (Bradham et al., 2011, 2015; Brattin et al., 2013; Juhasz et al., 2009, 2014a). Differences in the regression models developed by different labs are likely due to use of different animal bioassays for measuring RBA, interlab variation in IVBA measurement error, and variability in soil characteristics or As speciation of samples assayed by each lab. The use of different animal models to measure RBA is particularly important, because the intended application of the IVBA assay is for predicting RBA in humans. However, no animal models or IVBA assays have been evaluated directly for predicting RBA in humans, nor are such evaluations in humans feasible or likely to be undertaken in the near future. Rather than attempting to justify selection of a specific animal model, this analysis combined data from studies that used different animal models and different methods to estimate RBA. In the combined data, laboratory (representing the source of each data pair) was a significant variable in the regression model; however, additional variance in RBA explained by including laboratory was relatively small (6%), compared to 76% for the model with IVBA alone. The mouse and swine assays yielded similar results when applied to aliquots of the same soil samples (Juhasz et al., 2014b; Bradham et al., 2013), which provides further support for their inclusion in the meta-analysis. The predominant source of the As at the sites from which the samples were collected (ore or ore processing, pesticide application, or herbicide application) was also a significant explanatory variable in the regression model; however, it explained only

approximately 3% of the variance in RBA. This variation may reflect differences in As species related to the source of contamination (Bradham et al. 2013; Brattin et al. 2013).

The final weighted regression model is considered to be more robust than the OLS model because it incorporates uncertainty in the individual estimates of RBA and IVBA. The weighted model is based on a large ($n = 83$) sample set that includes soils affected by various As waste processes, including mining, smelting, and pesticide or herbicide application (Table S-1), and data from three different RBA bioassays. By combining data from multiple studies, the model incorporates interlab variability in the IVBA–RBA relationship, thereby providing more realistic prediction limits for RBA, which are important considerations in risk assessment. Given the size and breadth of the sample sources, we postulate that new data are unlikely to alter the regression parameter estimates appreciably; however, the model may be updated and reevaluated as new IVBA–RBA data become available. Of particular interest would be paired RBA and IVBA measurements for additional soils that might serve as a validation data set, allowing comparison of predicted and measured RBA in a set of soils that were not included in data used to derive the regression model.

This analysis relied completely on in situ contaminated soils and excluded spiked samples that were created by addition of sodium arsenate to a site soil. This approach was utilized because the regression model is intended for use in predicting As RBA of soils found at sites where contamination may have been in place for many years or decades, whereas IVBA and RBA measures of spiked soils may change with aging depending on the physical–chemical properties of the soil (Brattin et al., 2013; Juhasz et al., 2007a, 2007b, 2009). Moreover, soils spiked with sodium arsenate usually display IVBA and RBA values close to 100%, which is higher than typically found at sites of contamination. A compilation and analysis of soil As RBA estimates that included more than 100 in situ contaminated soils collected from a wide variety of metal contaminated sites found that the 95th percentile RBA was 60% (U.S. EPA, 2012a). The 95th percentile



RBA for the pooled data used in this analysis was 54.3% and the highest RBA was 80.5%. Excluding sodium arsenate spiked samples from the analysis yielded a regression model that is more representative of As RBA likely to be encountered at most contaminated sites.

The observation of one influential outlier in data collected for this analysis suggests that 0.4 M/pH 1.5 IVBA assay may not reliably predict RBA in every soil. In this case, the soil sample (number 34 in Supplemental Data, Table S-1) exhibited an IVBA (41.7%) that was sixfold higher than its RBA (6.8%). The soil was collected from a site affected by historical arsenate pesticide applications. However, this was not the sole contributing factor to the large IVBA/RBA ratio, because 17 other pesticide sites did not display large IVBA/RBA ratios (range 0.4–1.3). Presumably, the large IVBA/RBA ratio arose from yet-to-be identified factors unique to this soil that influence As absorption and are not accounted for by IVBA assay. Although only 1 of 84 soil samples included in this analysis was a statistical outlier, an important future objective would be to gather more information on such soils to identify measurable soil or As characteristics that might help identify samples that may not be well-represented by the current model.

The regression model based on the pooled data provides strong support for the 0.4 M glycine/pH 1.5 IVBA assay (U.S. EPA, 2012c) to predict oral RBA of As in soil. The IVBA method was shown in multiple labs to provide a strong correlation with RBA (Bradham et al., 2011, 2015; Brattin et al., 2013; Juhasz et al., 2009; 2014a) and demonstrated excellent interlab reproducibility (Brattin et al., 2013). The 0.4 M glycine/pH 1.5 IVBA assay has several important attributes that make it highly suitable for risk assessment. In addition to reliably predicting in vivo RBA, it is a relatively simple assay that does not require special lab equipment other than a means for monitoring pH and agitating samples at 37°C. Laboratories that are qualified to run EPA Standard Operating Procedure 9200.2-86 (U.S. EPA, 2012c) have all the necessary apparatus for performing soil extractions. The extraction protocol is identical to that employed in the IVBA assay, which EPA has validated for

predicting the RBA of lead in soil for human health risk assessment (U.S. EPA, 2007b). Adoption of this extraction protocol as a standard protocol for As enables RBA estimates for lead and As to be obtained in a single extraction of the same soil sample, potentially realizing a cost savings at sites where lead and As are co-contaminants in soil.

Disclaimer

The U.S. Environmental Protection Agency funded and managed the research described here. It has been subjected to agency review and approved for publication. No attempt was made to validate data in the cited literature. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

- Becker, B.J., and Wo, M. 2007. The synthesis of regression slopes in metal-analysis. *Stat. Sci.* 22: 414–429.
- Bradham, K. D., Scheckel, K. G., Nelson, C. M., Seales, P. E., Lee, G. E., Hughes, M. F., Miller, B. W., Yeow, A., Gilmore, T., Serda, S. M., Harper, S., and Thomas, D. J. 2011. Relative bioavailability and bioaccessibility and speciation of arsenic in contaminated soils. *Environ. Health Perspect.* 119: 1629–1634.
- Bradham, K. D., Diamond, G. L., Scheckel, K. G., Hughes, M. F., Casteel, S. W., Miller, B. W., Klotzbach, J. M., Thayer, W. C., and Thomas, D. J. 2013. Mouse assay for determination of arsenic bioavailability in contaminated soils. *J. Toxicol. Environ. Health A* 76: 815–826.
- Bradham, K. D., Nelson, C., Juhasz, A. L., Smith, E., Scheckel, K., Obenour, D. R., Miller, B. W., and Thomas, D. J. 2015. Independent data validation of an in vitro method for the prediction of the relative bioavailability of arsenic in contaminated soils. *Environ. Sci. Technol.* 49: 6313–6318.
- Brattin, W., and Casteel, S. 2013. Measurement of arsenic relative bioavailability in swine. *J. Toxicol. Environ. Health A* 76: 449–457.
- Brattin, W., Drexler, J., Lowney, Y., Griffin, S., Diamond, G., and Woodbury, L. 2013. An in vitro method for estimation of arsenic relative bioavailability in soil. *J. Toxicol. Environ. Health A* 76: 458–478.
- Denys, S., Caboche, J., Tack, K., Rycken, G., Wragg, J., Cave, M., Jondreville, C., and Feidt, C. 2012. *In vivo validation of the unified BARGE method to assess the bioaccessibility of arsenic, antimony, cadmium, and lead in soils.* *Environ. Sci. Technol.* 46: 6252–6260.

- Drexler, J. W., and Brattin, W. J. 2007. An *in vitro* procedure for estimation of lead relative bioavailability: With validation. *Hum. Ecol. Risk Assess.* 13: 383–401.
- Juhasz, A. L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Sansom, L., and Naidu, R. 2007a. *In vitro* assessment of arsenic bioaccessibility in contaminated (anthropogenic and geogenic) soils. *Chemosphere* 69: 69–78.
- Juhasz, A. L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Sansom, L., and Naidu, R. 2007b. Comparison of *in vivo* and *in vitro* methodologies for the assessment of arsenic bioavailability in contaminated soils. *Chemosphere* 69: 961–966.
- Juhasz, A. L., Weber, J., Smith, E., Naidu, R., Rees, M., Rofe, A., Kuchel, T., and Sansom, L. 2009. Assessment of four commonly employed *in vitro* arsenic bioaccessibility assays for predicting *in vivo* relative arsenic bioavailability in contaminated soils. *Environ. Sci. Technol.* 43: 9487–9494.
- Juhasz, A. L., Weber, J., and Smith, E. 2011. Predicting arsenic relative bioavailability in contaminated soils using meta-analysis and relative bioavailability – Bioaccessibility regression models. *Environ. Sci. Technol.* 45: 10676–10683.
- Juhasz, A. L., Herde, P., Herde, C., Boland, J., and Smith, E. 2014a. Validation of the predictive capabilities of the Sbrc-G *in vitro* assay for estimating arsenic relative bioavailability in contaminated soils. *Environ. Sci. Technol.* 48: 12962–12969.
- Juhasz, A. L., Smith, E., Nelson, C., Thomas, D. J., and Bradham, K. 2014b. Variability associated with As *in vivo*-*in vitro* correlations when using different bioaccessibility methodologies. *Environ. Sci. Technol.* 48: 11646–11653.
- Makris, K. C., Quazi, S., Nagar, R., Sarkar, D., Datta, R., and Sylvia, V. L. 2008. *In vitro* model improves the prediction of soil arsenic bioavailability: Worst-case scenario. *Environ. Sci. Technol.* 42: 6278–6284.
- Medlin, E. A. 1997. An *in vitro* method for estimating the relative bioavailability of lead in humans. Master's thesis, Department of Geological Sciences, University of Colorado, Boulder, CO.
- Press, W. H., Teukolsky, S. A., Vetterling, W. T., and Flannery, B. P. 1992. *Numerical recipes in C. The art of scientific computing*. New York, NY: Cambridge University Press.
- Rees, M., Sansom, L., Rofe, A., Juhasz, A. L., Smith, E., Weber, J., Naidu, R., and Kuchel, T. 2009. Principles and application of an *in vivo* swine assay for the determination of arsenic bioavailability in contaminated matrices. *Environ. Geochem. Health* 31: 167–177.
- Roberts, S. M., Munson, J. W., Lowney, Y. W., and Ruby, M. V. 2007. Relative oral bioavailability of arsenic from contaminated soils measured in the cynomolgus monkey. *Toxicol. Sci.* 95: 281–288.
- Rodriguez, R. R., Basta, N. T., Casteel, S. W., and Pace, L. W. 1999. An *in vitro* gastrointestinal method to estimate bioavailable arsenic in contaminated soils and solid media. *Environ. Sci. Technol.* 33: 642–649.
- Ruby, M. W., Davis, A., Schoof, R., Eberle, S., and Sellstone, C. M. 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environ. Sci. Technol.* 30: 422–430.
- Ruby, M. V., Schoof, R., Brattin, W., Goldage, M., Post, G., Harnois, M., Mosby, D. E., Casteel, S.W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., and Chappell, E. 1999. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ. Sci. Technol.* 33: 3697–3705.
- Scheckel, K. G., Chaney, R. L., Basta, N. T., and Ryan, J.A. 2009. Advances in assessing bioavailability of metal(lloid)s in contaminated soils. *Adv. Agron.* 104: 1–52.
- Thirumalai, K., Singh, A., and Ramesh, R. 2011. A MATLAB™ code to perform weighted linear regression with (correlated or uncorrelated) error in bivariate data. *J. Geol Soc. India.* 77: 377–380.
- U.S. Environmental Protection Agency. 1989. *Risk assessment guidance for Superfund (RAGS). Volume I. Human health evaluation manual (Part A)*. Washington, DC: U.S. Environmental Protection Agency, Office of Emergency and Remedial Response. EPA/540/1-89/002. December. http://www.epa.gov/superfund/riskassessment/ragsa/pdf/rags-voll-pt1_complete.pdf
- U.S. Environmental Protection Agency. 2007a. Framework for metals risk assessment. Washington, DC: U.S. Environmental Protection Agency, Office of the Science Advisor. EPA 120/R-07/001. <http://www.epa.gov/raf/metalsframework/pdfs/metals-risk-assessment-final.pdf>
- U.S. Environmental Protection Agency. 2007b. Guidance for evaluating the oral bioavailability of metals in soils for use in human health risk assessment. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. OSWER 9285.7-80. http://www.epa.gov/superfund/health/contaminants/bioavailability/bio_guidance.pdf
- U.S. Environmental Protection Agency. 2007c. Method 6010c. <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6010c.pdf>
- U.S. Environmental Protection Agency. 2007d. Method 6020A. <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6020a.pdf>
- U.S. Environmental Protection Agency. 2012a. Compilation and review of data on relative bioavailability of arsenic in soil. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. OSWER 9200.1-113. <http://www.epa.gov/superfund/health/contaminants/bioavailability/guidance.htm>
- U.S. Environmental Protection Agency. 2012b. Recommendations for default value for relative bioavailability of arsenic in soil. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. OSWER 9200.1-113. <http://www.epa.gov/superfund/health/contaminants/bioavailability/guidance.htm>

- U.S. Environmental Protection Agency. 2012c. Standard operating procedure for an *in vitro* bioaccessibility assay for lead in soil. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. OSWER 9200.1-86. November. <http://www.epa.gov/superfund/health/contaminants/bioavailability/guidance.htm>
- Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., and Van der Wiele, T. 2011. An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium, and lead in soil. *Sci. Total Environ.* 409: 4016–4030.
- York, D., Evensen, M., Martinez, M., and Delgado, J. 2004. Unifies equations for the slope, intercept and standard errors of the best straight line. *Am. J. Phys.* 72: 367–375.

Professional Certification

I certify under penalty of law that this report and all attachments were prepared by me or under my direct supervision in accordance with the Voluntary Remediation Program Act (O.C.G.A. Section 12-8-101, et seq.). I am a professional engineer / professional geologist who is registered with the Georgia State Board of Registration for Professional Engineers and Land Surveyors / Georgia State Board of Registration for Professional Geologists and I have the necessary experience and am in charge of the investigation and remediation of this release of regulated substances.

Furthermore, to document my direct oversight of the Voluntary Remediation Plan development, implementation of corrective action, and long term monitoring, I have attached a monthly summary of hours invoiced and description of services provided by me to the Voluntary Remediation Program participant since the previous submittal to the Georgia Environmental Protection Division.

The information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Andrew P. Romanek, P.E.
Associate
CDM Smith

Date

Summary of Oversight Provided by Georgia Licensed Engineers and Geologists

Engineer / Geologist	License Type and No.	Week Ending Date	Number of Hours	Description of Hours
Tom Duffey	Geologist PG000899	1/9/16	0.5	Senior hydrogeologist and technical lead. Involved in discussions and evaluations regarding remedial action.
		4/30/16	5	
John Reichling	Engineer PE017367	1/9/16	1	CDM Smith Officer in Charge and person overall responsible for project execution and quality.
Andrew Romanek	Engineer PE029287	1/9/16	2.5	Project manager and CDM Smith primary point of contact. Involved in all aspects of the project, including evaluation of remedial action options.
		4/30/16	0.5	